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The structure of Si(112):Ga-($N \times 1$) reconstructions

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Abstract

We have studied the structure of Si(112):Ga-($N \times 1$) reconstructions using atomic-resolution scanning tunneling microscopy and first-principles calculations. The nanofaceted clean Si(112) surface becomes planar following the adsorption of Ga, which forms long chains on the surface interrupted by isolated quasi-periodic defects. The defects create a mixture of ($N \times 1$) structures ($N \approx 4$–7) with 5×1 and 6×1 unit cells most common. We demonstrate that this structure consists of a chain of Ga atoms adsorbed at the (111)-like step edge within the (112) unit cell, and that the defects are Ga vacancies where the exposed step edge Si atoms form a dimer bond. Calculations performed as a function of vacancy period confirm that the surface energy is minimized at $N = 5$–6, when compressive strain associated with the Si–Ga bonds is effectively minimized.

Keywords: Density functional calculations; Gallium; High index single crystal surfaces; Scanning tunneling microscopy; Silicon; Surface energy; Surface structure, morphology, roughness, and topography

A variety of systems have been explored as candidates for the growth of self-assembled wires on the nanometer scale. For example, V-shaped grooves have been used as templates for growing quantum wire arrays [1], and vicinal surfaces have been used to nucleate atomically thin wires at the step edges [2]. In these systems it is generally assumed that the substrate is structurally inert – that is, the known morphology of the surface determines the geometry of the heterostructure, with the self-assembly governed by interactions within the overlayer. Based on a variety of experiments over the past two decades, the adsorption of Ga on Si(112) has been described as such a step edge 'atomic-wire' system [3–7]. However, it was recently shown that clean Si(112) is faceted [8], and only becomes planar following the adsorption of Ga [9]. This large-scale surface restructuring indicates that Ga interacts strongly with the substrate, and therefore the self-assembly in this case is a fundamentally different phenomenon.

The bulk-terminated Si(112) surface consists of narrow (111) terraces [two (1×1)-unit cells wide] separated by single-height steps, and it has long been asserted that Ga 'wires' adsorb along the step edges [4–7]. As shown by scanning tunneling microscopy (STM), the clean Si(112) surface consists of quasi-periodic nanofacets ($\sim$10 nm width) with (111) and $\sim$(337) orientations [8]. Following Ga adsorption and annealing, the surface morphology becomes planar [i.e. all terraces have a (112)

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14. ABSTRACT

We have studied the structure of Si(112):Ga-(N×1) reconstructions using atomic-resolution scanning tunneling microscopy and first-principles calculations. The nanofaceted clean Si(112) surface becomes planar following the adsorption of Ga, which forms long chains on the surface interrupted by isolated quasi-periodic defects. The defects create a mixture of (N×1) structures (N#4-7) with 5×1 and 6×1 unit cells most common. We demonstrate that this structure consists of a chain of Ga atoms adsorbed at the (111)-like step edge within the (112) unit cell, and that the defects are Ga vacancies where the exposed step edge Si atoms form a dimer bond. Calculations performed as a function of vacancy period confirm that the surface energy is minimized at N=5-6, when compressive strain associated with the Si-Ga bonds is effectively minimized.

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orientation] with a mixture of (5×1) and (6×1) structures. It has been proposed that the $(N\times1)$ periodicity is caused by periodic vacancies within the Ga chains [4–7]. In this Letter, we use both STM and first-principles total-energy calculations to show definitively that this vacancy model is indeed correct.

The STM experiments were performed in ultra-high vacuum using Si wafers oriented to within 0.5° of (112). To obtain a clean surface each sample was radiatively heated to 1150°C for 60 s (pressure $\leq 2\times10^{-9}$ Torr). Gallium was deposited from a heated tungsten basket onto samples at temperatures below 150°C. After depositing >1 ML of Ga, the surface was annealed to 500 ± 50°C for 10 min, resulting in a '6×1' low energy electron diffraction (LEED) pattern thought to correspond to 5/6 Ga atoms per bulk-terminated (112) unit cell [5,7]. The Auger electron spectroscopy (AES) Ga (55 eV)-to-Si (92 eV) peak height ratio on this surface was 0.04 ± 0.005, similar to that observed previously [4], indicating that we produced a comparable surface structure. STM images of the filled and empty electronic states were acquired at room temperature with a constant current between 0.1 and 0.3 nA and bias voltages between 1.0 and 2.5 V.

Fig. 1 shows gray-scale STM images of the Si(112):Ga-$(N\times1)$ surface exhibiting well-ordered row structures oriented along the $[\bar{1}10]$ direction. The spacing between rows is 0.94 nm, corresponding to the width of the bulk-terminated (112) unit cell, confirming the local restoration of the basal orientation. Along these rows, isolated periodic defects are observed that appear as dark minima in empty-state images and slightly enhanced maxima in filled-state images. The single defects are correlated across the rows and resemble trenches perpendicular to the row direction in the empty states. At higher magnification [Fig. 1c,d and Fig. 2], the filled-state 'bumps' range in appearance from symmetrical pairs of weak maxima to more pronounced single maxima. Similarly, in the empty states some defects appear as single depressions along the row, and others as wider, asymmetrical depressions. Within a single row the separation between these defects varies from $4a$ to $7a$ ($a=0.34$ nm, the length of the bulk-terminated unit cell in the $[\bar{1}10]$ direction). Previous LEED studies have found that Ga/Si(112) exhibits both (5×1) and (6×1) reconstructions [4,5,7]. From our STM results it is clear that there is actually a range of 'local periodicities' fluctuating around an average value between $5a$ and $6a$.

Identifying the defects requires a structural model for the Ga adsorption. A model was first suggested by Jung et al. [5], based on LEED and AES, in which Ga adsorbs at the step edge within each bulk-terminated (112) unit cell to form Ga chains. The observed (6×1) reconstruction was interpreted as one-sixth Ga vacancies, which leave unbonded pairs of Si step edge atoms to rebond as dimers, as shown in Fig. 2. A subsequent angle-resolved AES study provided structural data supporting this model [6]. This model has the attractive feature that it immediately explains the absence of adjacent defects in the STM images: two adjacent vacancies would necessarily lead to a Si dimer plus a Si step edge atom with two dangling bonds – an energetically unfavorable geometry. However, the atomic-resolution STM images cannot easily be interpreted in terms of this structure given that 'bumps' are observed in the filled states where a vacancy is supposed to lie. In order to determine the structure definitively, we have performed extensive first-principles total-energy calculations.

The calculations were performed in a (112) slab geometry with six layers of Si and a vacuum layer equivalent to five layers of Si, with the same single $(N\times1)$ unit cell on both slab surfaces. Total energies and forces were calculated within the local-density approximation (LDA) with gradient corrections [10], using Troullier–Martins pseudopotentials and a plane-wave basis with a kinetic energy cutoff of 8 Ry, as implemented in the FHI96MDcode [11]. Because the surface Brillouin zones of the different supercells are not simply related, the individual total energies were required to be completely converged with respect to k-point sampling. Most importantly, full structural relaxation was performed on all but the innermost two layers until the surface energies were converged to 0.1 meV Å^{-2}. A variety of structural models were investigated, including Ga adsorbed on the (111)

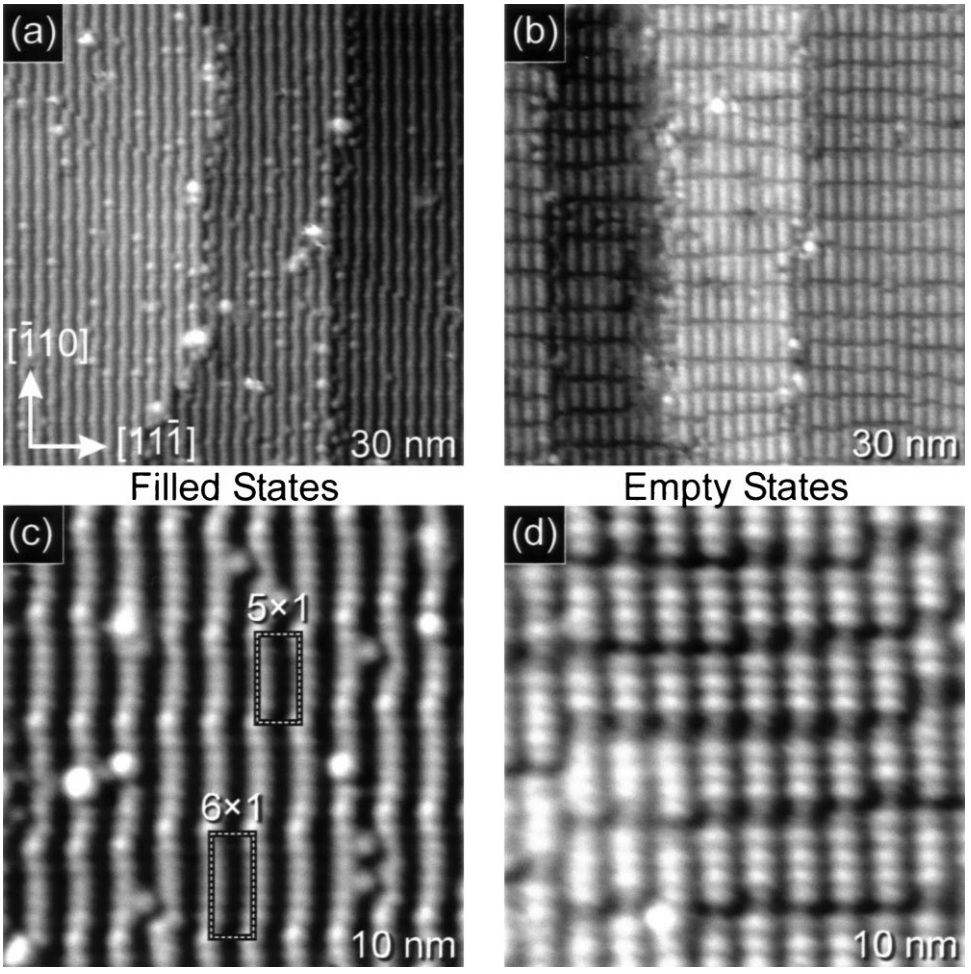

Fig. 1. Gray-scale STM images of Si(112):Ga-($N\times1$) measured for both the filled (a,c) and empty (b,d) states on different areas of the surface. The size of each image is indicated. The ($N\times1$) reconstruction appears as rows oriented along the [$\bar{1}$10] direction interrupted by quasi-periodic defects that are correlated along [11$\bar{1}$] (N ranges from 4 to 7, but is most often 5 or 6). The defects appear as deep trenches in the empty state topography and as slight ridges in the filled states. Note that the images in (a) and (b) include multiple (112) terraces.

terraces in T_4 or atop sites, and along the step edges with periodic vacancies or substitutional Si atoms within the chain. In the end, the step edge/vacancy model had the lowest surface energy and was the only structure consistent with the STM images.

Within the ($N\times1$) step edge/vacancy model we examined a wide range of vacancy periods, with N ranging from 2 (every other Ga atom missing) to 8, as well as a (1×1) structure with no vacancies (equivalent to $N\to\infty$). In order to compare the relative stability of the different vacancy periodicities, we computed the equilibrium surface free energy per unit area, $\gamma(\theta)$, as a function of the Ga coverage, $\theta=(N-1)/N$:

$$\gamma(\theta)=(2A)^{-1}[E_t(\theta)-n_{Ga}E_{Ga}-n_{Si}E_{Si}] \quad (3)$$

where A is the surface area of the ($N\times1$) unit cell, $E_t(\theta)$ the total energy, $n_{Ga,Si}$ the number of atoms per cell, and $E_{Ga,Si}$ the chemical potentials. Note that we are only interested in relative surface energies, which depend on the chemical potential

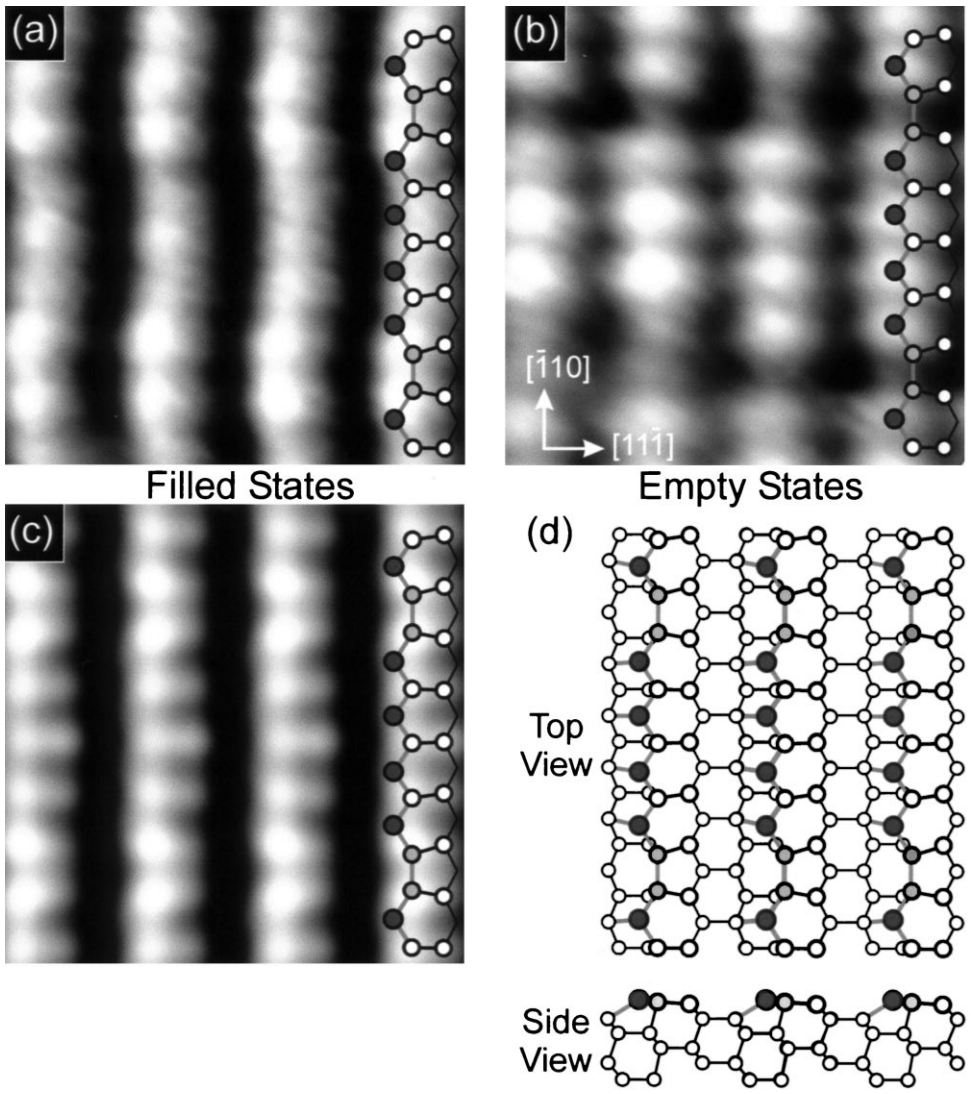

Fig. 2. Atomic-resolution dual-bias STM image of the (a) filled and (b) empty states in one (5×1) area. (c) Simulated filled-state image calculated for a (5×1) step edge/vacancy model where the adjacent Si atoms at the vacancy site form a dimer. (d) Model for the Si(112):Ga-(5×1) reconstruction after full structural relaxation. Ga atoms are dark gray and rebonded Si dimer atoms are lighter gray.

of Ga but not of Si in this case. For E_{Ga} we use here the calculated energy per atom of bulk Ga, which is the thermodynamic upper limit for E_{Ga}; the minimum of $\gamma(\theta)$ is unchanged for E_{Ga} within $\sim$1 eV of this limit. As shown in Fig. 3, where we compare the relative energies with respect to that for no vacancies, a sharply defined minimum in the calculated surface energy occurs for (5×1) and (6×1) vacancy periods, in remarkable agreement with the average spacing observed experimentally. Because each calculation was limited to a single $(N\times1)$ unit cell, we cannot comment on the energetics of the vacancy alignment from row-to-row.

One puzzling feature of this surface is the appearance of the vacancy defects as raised

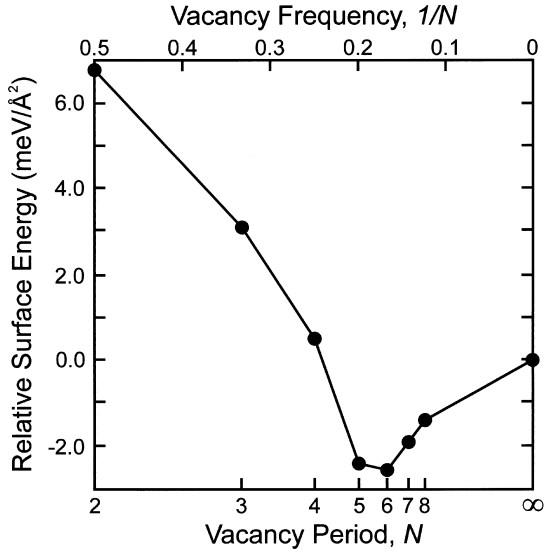

Fig. 3. First-principles surface energies calculated as a function of vacancy period. The energy, displayed relative to the energy for continuous Ga chains (no vacancies), is lowest for (5×1) and (6×1) periods, in agreement with experiment.

'bumps' in the filled-state topography. This apparent contradiction is neatly resolved by analyzing our numerically simulated constant-current STM images of the ground-state structure – which also show raised bumps at the defect sites (see Fig. 2). From the spatial relationship between the simulated topography and the underlying atomic positions, it is clear that all of the maxima are associated with Si atoms; that is, the Ga atoms do not appear in the filled-state image. Thus, the vertical row structures seen in Fig. 1a,c and Fig. 2a are not adsorbed Ga atoms but rather Si step edge atoms, and the raised features are associated with the dimer-bonded Si atoms at each vacancy site. Finally, although the dimers appear higher than the step edge atoms in the images, they are physically slightly lower. Their apparently raised height is a purely electronic effect: because the Si dimer bond is highly strained, the associated surface state is closer to the Fermi level, causing a relative increase in the local state density and a 'bump' in the filled-state topography. The electronic structure of the empty state surface is relatively simpler, dominated by state density localized above each Ga atom (not shown), in agreement with experiment. We assume the variable appearance of the defects in the room-temperature images is associated with higher-energy, asymmetrical variations in the local vacancy structure.

Our first-principles results not only correctly predict the ground-state equilibrium (5×1) and (6×1) structures, but also provide insight into the physical mechanism that leads to their relative stabilities. When there are no Ga vacancies, the fully relaxed surface geometry shows that the step edge Si–Ga bond is compressed by 7% relative to a terrace Si–Ga bond length. Introducing widely separated vacancies relieves this compression, but only in the vicinity of the resulting Si dimer. With more frequent vacancies, a larger fraction of these compressed Si–Ga bonds is relieved; hence, Si–Ga strain relief favors having the vacancies close together. However, when the vacancies become two to three lattice constants apart, the average strain in the Si–Ga chains changes from compressive to tensile, leading to an effective short-range vacancy repulsion. The resolution of these competing interactions at $N=5$–6 is a function of the effective Si–Ga force constant and the substrate Si lattice constant, and can be described analytically by a one-dimensional Frenkel–Kontorova model (as will be reported in a separate publication [12]).

In conclusion, we have studied the structure of Si(112):Ga-$(N\times1)$ reconstructions using atomic-resolution scanning tunneling microscopy (STM) and first-principles calculations. We demonstrate that the $(N\times1)$ structure consists of a chain of Ga atoms adsorbed at the (111)-like step edge within the (112) unit cell, interrupted by periodic vacancies where the exposed step edge Si atoms form a dimer bond, as previously proposed. Calculations performed as a function of vacancy period confirm the surface energy is minimized at $N=5$–6, when the strain energy associated with the Si–Ga bonds is effectively minimized. Given the multilayer restructuring of the Si(112) surface that occurs upon adsorption of Ga, this system would be more accurately described as an adsorbate-induced surface reconstruction rather than a self-assembled array of 'quantum wires'. It has recently been shown that the optical reflectivity of this surface has a significant directional anisotropy [7], and we expect the chain-like structure of the Ga overlayer

to give rise to other unusual electronic and optical properties as well.

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